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- (54) **PACKAGING AND METHODS OF USE FOR RESPIRING BIOLOGICAL MATERIALS**
- (71) Applicant: **Apio, Inc.**, Guadalupe, CA (US)
- (72) Inventor: **Raymond Clarke**, Los Altos, CA (US)
- (73) Assignee: **Curation Foods, Inc.**, Santa Maria, CA (US)
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See application file for complete search history.

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Primary Examiner — Erik Kashnikow

- (57) **ABSTRACT**

Packaging of fruits in containers. The containers preferably have designed permeabilities to oxygen, carbon dioxide, and ethylene and include a gas-permeable membrane comprising (1) a microporous film, and (2) a polymeric coating on the microporous film. The containers enable storage and/or ripening of fruits under controlled conditions. Using the new containers, fruits can be ripened while they are being transported, or in conventional ripening rooms without opening the bags in which they have been transported. In addition, fruits can be preserved in a satisfactory ripened state for longer periods of time. Methods of treating fruits with insecticides, fungicides and mold-inhibiting compounds are also disclosed.

5 Claims, No Drawings

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PACKAGING AND METHODS OF USE FOR RESPIRING BIOLOGICAL MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of co-pending, commonly assigned, application Ser. No. 13/368,216, filed Feb. 7, 2012. Application Ser. No. 13/368,216, filed Feb. 7, 2012 is a continuation of Ser. No. 09/858,190, filed May 15, 2001, now U.S. Pat. No. 8,110,232. Ser. No. 09/858,190 is also related to claims priority under 37 CFR 1.78(a)(5) from Provisional Application Ser. No. 60/325,762, filed May 26, 2000, which resulted from the conversion of application Ser. No. 09/580,379, into a provisional application under 37 CFR 1.53(c)(2). This application is also related to (1) application Ser. No. 09/989,682, filed Nov. 20, 2001, now U.S. Pat. No. 7,601,374, which is a continuation-in-part of Ser. No. 09/858,190, and (2) application Ser. No. 12/553,852 filed Sep. 3, 2009, now U.S. Pat. No. 8,092,848, which is a divisional of Ser. No. 09/989,682. The entire disclosure of each of those patents and applications is incorporated herein by reference for all purposes.

BACKGROUND OF THE INVENTION

This invention relates to the packaging of respiring biological materials.

Respiring biological materials, e.g. fruits and vegetables, consume oxygen (O_2) and produce carbon dioxide (CO_2) at rates which depend upon the stage of their development, the atmosphere surrounding them and the temperature. In modified atmosphere packaging (MAP), the objective is to produce a desired atmosphere around respiring materials by placing them in a sealed container whose permeability to O_2 and CO_2 is correlated with (i) the partial pressures of O_2 and CO_2 in the air outside the package, and (ii) the temperature, to produce a desired atmosphere within the container. In many cases, the container includes an atmosphere control member having a high permeability to O_2 and CO_2 . In controlled atmosphere packaging (CAP), the objective is to produce a desired atmosphere around respiring materials by displacing some or all of the air within a container by one or more gases, e.g. nitrogen, O_2 , CO_2 and ethylene, in desired proportions. Reference may be made, for example, to U.S. Pat. No. 3,360,380 (Bedrosian), U.S. Pat. No. 3,450,542 (Badran), U.S. Pat. No. 3,450,544 (Badran et al.), U.S. Pat. No. 3,798,333 (Cummin et al), U.S. Pat. No. 3,924,010 (Erb), U.S. Pat. No. 4,003,728 (Rath), U.S. Pat. No. 4,734,324 (Hill), U.S. Pat. No. 4,779,524 (Wade), U.S. Pat. No. 4,830,863 (Jones), U.S. Pat. No. 4,842,875 (Anderson), U.S. Pat. No. 4,879,078 (Antoon), U.S. Pat. No. 4,910,032 (Antoon), U.S. Pat. No. 4,923,703 (Antoon), U.S. Pat. No. 4,987,745 (Harris), U.S. Pat. No. 5,041,290 (Wallace et al.) U.S. Pat. No. 5,045,331 (Antoon), U.S. Pat. No. 5,063,753 (Woodruff), U.S. Pat. No. 5,160,768 (Antoon), U.S. Pat. No. 5,254,354 (Stewart), U.S. Pat. No. 5,333,394 (Herdeman), U.S. Pat. No. 5,433,335 (Raudalus et al.), U.S. Pat. No. 5,460,841 (Herdeman), U.S. Pat. No. 5,556,658 (Raudalus et al.), U.S. Pat. No. 5,658,607 (Herdeman), U.S. Pat. No. 6,013,293 (De Moor) and U.S. Pat. No. 6,376,032 (Clarke et al), International Publication Nos. WO 94/12040 (Fresh Western) and WO 00/04787 (Landec), and European Patent Applications Nos. 0,351,115 and U.S. Pat. No. 0,351,116 (Courtaulds). The disclosure of each of these patents and publications is incorporated herein by reference.

U.S. Pat. No. 6,376,032 discloses that a membrane which comprises a microporous film and a polymeric coating on the microporous film, has an oxygen permeability (OTR), at all temperatures between 20° and 25° C., of at least 775,000 ml/m² .atm.24hrs (50,000ml/100 in.².atm.24hrs), for example 775,000 to 7,750,000 ml/m² .atm.24hrs, preferably 1,550,000 to 3,875,000 ml/m² .atm.24hrs. U.S. Pat. No. 6,376,032 discloses that this membrane can be used to control the atmosphere within a sealed container whose walls are relatively impervious to gases except over one or more control sections which are provided by such a membrane, and that the membrane can extend across a complete dimension of the sealed container. U.S. Pat. No. 6,376,032 also discloses that the size of the container can vary considerably and can contain for example up to 1500 lb (680 kg) of produce.

The preferred packaging atmosphere for a respiring material often depends on the age of the material and the changes (if any) in the material which are desired. Generally, for example, the preferred O_2 content during storage of unripe fruits is lower than the preferred O_2 content during subsequent ripening at a higher temperature. This fact causes problems for both MAP and CAP. For example, in MAP, although the O_2 permeability of the container generally increases with temperature (especially if it contains an atmosphere control member comprising a crystalline polymer having an appropriate melting point, as disclosed in U.S. Pat. No. 6,376,032 and International Publication No. WO 00/04787), the increase is often insufficient to avoid the need for significant compromise between the preferred atmospheres at different stages. In CAP, it is theoretically possible to monitor the packaging atmosphere and to change it as often as is necessary to maintain the preferred level of O_2 (and other gases). But this is difficult and expensive, and often impractical.

For example, U.S. Pat. No. 5,799,495 discloses a system in which biologically respiring material, e.g. fruit, is transported and ripened in a sealed container, and is first surrounded by a first atmosphere and thereafter by a second atmosphere, the second atmosphere containing more oxygen than the first. The atmospheres are controlled by injection of appropriate gases directly into the container.

Many fruits are picked when they are unripe; transported and stored under conditions which prevent or retard ripening; and ripen shortly before sale. Many fruits ripen more rapidly when exposed to ethylene, and some (e.g. bananas, tomatoes, avocados, Bartlett pears, kiwis, melons, peppers and mangos) are ripened commercially by exposure to ethylene in ripening rooms. When the fruits have been placed in a sealed bag or other container for transport or storage, the container is opened to expose the fruits to the ethylene. Another problem associated with the use of ripening rooms is that the fruits can ripen too rapidly, especially when the fruits ripen through a climacteric and therefore undergo a very large increase in respiration rate and generate heat in the ripening room.

Bananas are respiring biological materials whose storage and ripening present the most serious problems because

- (i) bananas are grown in locations far distant from the locations at which they are consumed;
- (ii) they are damaged by storage at temperatures below about 14.4° C., with the extent of the damage depending upon the time spent below that temperature and how far the temperature is below 14.4° C. (58° F.);
- (iii) they go through a climacteric when they ripen, thus producing a very large increase in respiration rate and the generation of heat;

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(iv) they generate ethylene as they ripen, and they ripen at a rate which increases with the concentration of ethylene around them—as a result, a single prematurely ripe banana can trigger premature ripening of many others; and

(iv) once they have ripened, and have been exposed to air, they rapidly become overripe.

These problems have not yet been solved. The conventional procedure is to harvest the bananas when they are hard, green and unripe; to transport the green bananas, at 13-14° C., to the location where they will be consumed; to ripen the green bananas by exposing them to ethylene in a ripening room at that location; and to place the ripened bananas on sale. The time at which the bananas are harvested depends on the time needed to transport them to the point-of-sale. Thus bananas are typically harvested at week 11 (i.e. 11 weeks after the flower emerges from the plant) or week 12. The green bananas are shipped in bags made of polyethylene about 0.04 to 0.06 mm (1.5-2.5 mil) thick, with each bag containing about 18 kg (40 lb) of bananas and being supported by a cardboard box. In many cases, after the bananas have been placed in the bag, most of the air is exhausted from the bag, and the bag is sealed; this is the procedure generally described in U.S. Pat. No. 3,450,542 (Badran). In other cases, the bag contains vent holes.

This conventional procedure suffers from a number of problems, for example:

(1) The need to harvest the bananas a good while before they are fully grown. It would be desirable to harvest the bananas at a later time, when they are larger. However, the later the bananas are picked, the greater the propensity for their climacteric to be triggered by small concentrations of ethylene, and experience has shown that if the bananas are harvested later than the presently established timetables, this results in prematurely ripe bananas when the bananas are shipped in vented bags, and in so-called “green-ripe” bananas when the bananas are shipped in sealed bags. Green-ripe bananas soften, but remain green, and have an unpleasant flavor.

(2) If, as in most cases, the bananas are shipped in sealed bags, it is necessary to open each of the shipping bags in order to ripen the green bananas by exposing them to ethylene.

(3) Bananas ripen very quickly, which heats the bananas excessively and/or increases the demand on the refrigeration equipment used to call the ripening room.

(4) The bananas, once ripened, must be sold within a few days, or scrapped.

SUMMARY OF THE INVENTION

A first area of the present invention is based on my realization that for bananas and other fruits which ripen when exposed to ethylene, one or more of the problems noted above can be mitigated or overcome by ripening the fruits within a sealed container which provides a pathway for oxygen, carbon dioxide and ethylene to enter or leave the container. The fruits can be ripened by exposing them to ethylene which (i) enters the container from an ethylene-containing atmosphere adjacent to the sealed container and/or (ii) is generated within the sealed container.

A second area of the present invention is concerned with situations in which the preferred packaging atmosphere has a zero or relatively low content of a particular gas during one stage and a relatively high content of that gas during another stage. In particular a relatively low oxygen content during one stage and a relatively high oxygen content during

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another stage. I have realized that in such situations, valuable results can be obtained by combining the techniques of MAP and CAP. For example a container having a high oxygen permeability can be placed either (i) in air when a packaging atmosphere of high oxygen content is desired or (ii) in a controlled atmosphere having a selected reduced oxygen content when a packaging atmosphere of low oxygen content is desired.

Some aspects of the present invention make use of both the first and second areas of the invention.

As noted above, some fruits generate ethylene as they ripen. Such ethylene is referred to herein as endogenous ethylene. The term “exogenous ethylene” is used herein to mean ethylene which is not derived from the fruits which are being ripened. Some other materials, for example acetylene, will also assist ripening of fruits which are ripened by exposure to ethylene. Reference may be made for example to Burg et al, Molecular Requirements for the Biological Activity of Ethylene, Plant Physiol (Lancaster) (1967) 42: 144-155, the disclosure of which is incorporated herein by reference. The term “ethylenic ripening agent” is used herein to mean ethylene or another substance which also assists ripening of fruits which can be ripened by exposure to ethylene. The abbreviation ERA is used herein for the term “ethylenic ripening agent”. The term “exogenous ERA” is used herein to mean ethylenic ripening agent which is not derived from the fruits which are being ripened.

The first area of the invention includes the following Aspects.

Aspect I.

A method of treating, e.g. storing and/or ripening, a respiring biological material, the method comprising

(A) providing a sealed package comprising

(a) a sealed container, and

(b) within the sealed container, (i) unripe fruits which ripen when exposed to ERA and (ii) a packaging atmosphere around the unripe fruits, the sealed container providing a pathway for oxygen, carbon dioxide and ERA to enter or leave the packaging atmosphere; and

(B) exposing the exterior of the sealed package to an atmosphere which contains exogenous ERA.

Aspect II.

A method of ripening fruits, the method comprising

(A) providing a sealed package which comprises

(a) a sealed container, and

(b) within the sealed container, (i) unripe fruits which ripen when exposed to ERA, (ii) a packaging atmosphere around the unripe fruits, and (iii) a source of exogenous ERA; the sealed container providing a pathway for oxygen, carbon dioxide and ERA to enter or leave the packaging atmosphere; and

(B) exposing the unripe fruits in the sealed package to exogenous ERA from the source of exogenous ERA in the sealed container.

Aspect III.

A sealed package which comprises

(a) a sealed container, and

(b) within the sealed container, (i) fruits, for example fruits which have ripened through a climacteric, (ii) a packaging atmosphere around the fruits, and (iii) exogenous ERA and/or a residue of exogenous ERA, the exogenous ERA and/or residue of exogenous ERA optionally being a gas which is part of the packaging atmosphere; the sealed container providing a pathway for oxygen, carbon dioxide and ERA to enter or leave the packaging atmosphere.

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Aspect IV.

A package which comprises

- (a) a container, the container being a sealed container or open container obtained by opening a sealed container, and
- (b) within the container, (i) fruits, and (ii) a packaging atmosphere around the fruits, the container, if it is sealed, providing a pathway for oxygen, carbon dioxide and ERA to enter or leave the packaging atmosphere, and if it is open, having provided a pathway for oxygen, carbon dioxide and ERA to enter or leave the packaging atmosphere when it was sealed; the container having one or both of the following characteristics
 - (i) the fruits therein have been ripened at least in part by exposing them to exogenous ERA, and
 - (ii) it contains the residue of a source of exogenous ERA.

For example, the container can be a sealed or open container in which the fruits have ripened through a climacteric as a result of exposure to ethylene in a ripening room or as a result of exposure to exogenous ERA generated within the container while it was sealed.

Aspect V.

A container, for example a shipping or trucking container, which may be a closed container or an open container which contains a plurality of sealed packages, each of the packages comprising:

- (a) a sealed container, and
- (b) within the sealed container, (i) fruits, for example fruits which have ripened through a climacteric or fruits which ripen through a climacteric, and (ii) a packaging atmosphere around the fruits; the sealed container providing a pathway for oxygen, carbon dioxide and ERA to enter or leave the packaging atmosphere; the container containing the plurality of sealed packages having at least one of the following features
 - (i) the packaging atmosphere in each of the sealed packages contains exogenous ERA and/or a residue of exogenous ERA;
 - (ii) at least some, and preferably each, of sealed packages contains exogenous ERA and/or a residue of exogenous ERA, the exogenous ERA and/or a residue of exogenous ERA, the exogenous ERA optionally being a gas which is part of the packaging atmosphere, or
 - (iii) the shipping or trucking or other container contains not only the sealed packages containing the fruits but also, not within any of the sealed packages, exogenous ERA and/or a residue of a source of exogenous ERA, the exogenous ERA and/or residue of a source of exogenous ERA optionally being a gas which is part of the atmosphere which contacts the exterior of the sealed packages.

The second area of the invention includes the following aspects.

Aspect VI.

A method of storing and/or ripening a respiring biological material, the method comprising

- (A) providing a sealed package comprising
 - (a) a sealed container, and
 - (b) within the sealed container, the respiring biological material; the sealed container providing a pathway for oxygen and carbon dioxide to enter or leave the packaging atmosphere;
- (B) exposing the exterior of the sealed package to a first atmosphere containing oxygen;
- (C) after step (B), exposing the exterior of sealed package to second atmosphere containing oxygen; the first and second atmospheres differing by at least 1% in their

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content of at least one gas which will pass through the container. Preferably there is a difference between the oxygen content of the first and second atmospheres of at least 3%.

The oxygen contents of the packaging atmosphere is in steps (B) and (C) will be lower than the oxygen contents of the atmosphere surrounding the package and any difference between them will be less than any difference between the oxygen contents of the first and second atmospheres. Preferably one of the first and second atmospheres is air.

This aspect of the invention is useful for the treatment of any respiring biological material, including but not limited to fruits (e.g. fruits which ripen through a climacteric, or unripe fruits which have ripened through a climacteric); and vegetables.

In one embodiment of the method of this aspect of the invention,

- (a) in step (B), the first controlled atmosphere is a controlled atmosphere having a reduced oxygen content, for example (i) less than 18% O₂, preferably less than 12% O₂, particularly less than 9% O₂, but (ii) more than 2% O₂, preferably more than 4% O₂, particularly more than 5% O₂, and the permeability of the container is such that the oxygen content of the packaging atmosphere is high enough to maintain respiration of the biological material (for example, in the case of unripe fruits, an oxygen content which is high enough to maintain respiration of the fruits, but low enough that the unripe fruits ripen slowly or not at all) and
- (b) in step (C), the second controlled atmosphere contains at least 3% more O₂ than the first atmosphere.

In this embodiment, when the package contains unripe fruits, the second atmosphere optionally contains exogenous ERA and is preferably air or a mixture of air and exogenous ERA. This results in an increase in the oxygen content of the packaging atmosphere thus assisting the unripe fruits to ripen.

In another embodiment of this aspect of the invention

- (a) the sealed packages containing fruits which initially are unripe,
- (b) in step (B), the first atmosphere is air and the permeability of the container is such that the oxygen contents of the packaging atmosphere is high enough to maintain respiration of fruits, but low enough that unripe fruits ripen slowly or not at all, and
- (c) in step (C), the second atmosphere contains at least 3% of oxygen and the first atmosphere preferably has an oxygen content of at least 24%, particularly at least 28%, thus increasing the oxygen content of the packaging atmosphere and assisting the unripe fruits to ripen.

In step (C), the second atmosphere contains at least 3% more oxygen than the first atmosphere, and preferably has an oxygen content of at least 24%, particularly at least 28% oxygen, thus increasing the oxygen content of the packaging atmosphere and assisting the unripe fruits to ripen.

In step (C), the fruits can if desired be exposed to exogenous ERA, for example by including exogenous ERA in the second atmosphere, and/or by including a source of exogenous ERA within the sealed package, and/or, when there are a plurality of packages in a large container, e.g. a shipping or trucking container, by including a source of ERA within the large container but outside the sealed packages. This embodiment of the invention can be used transport and ripen bananas in a sealed container, for example a conventional polyethylene bag, whose oxygen permeability is too

low to permit satisfactory ripening in the atmospheres used in conventional ripening rooms.

In these two embodiments, it is preferred that, during at least one period of step (B), the oxygen content of the packaging atmosphere reaches a value, which may be in equilibrium value, which is (i) more than 1%, preferably more than 2%, and (i) less than 7%, preferably less than 5%, particularly less than 3.5%.

In another embodiment of this aspect of the invention, the first and second atmospheres differ in their content of some gas other than oxygen which will pass through the sealed container, for example carbon dioxide or another gas having a desired effect on the respiring biological material, e.g. an insecticide, fungicide or a mold-inhibiting compound. One of the atmospheres can contain 0% of the gas other than oxygen. In this embodiment, the oxygen content of the first and second atmospheres can be the same or different. For example, this embodiment of the invention could be used to store the respiring material in the sealed package under preferred conditions during one of steps (B) and (C), and in the other step to use a controlled atmosphere to change the packaging atmosphere, for a relatively short time, to an atmosphere containing a desired amount of the gas other than oxygen, for example to contact the respiring material with an atmosphere containing a relatively high percentage of carbon dioxide, e.g. 15-30%, from a relatively limited period of time, e.g. for 5-48 or 15-30 hours. Such method would be useful, for example, for the treatment of broccoli to control aphids.

The invention is particularly useful for storage and/or ripening of bananas. Some embodiments of the invention make it possible to maintain bananas, before and/or after their climacteric, and a packaging atmosphere which enable storage and/or ripening of green bananas in a controlled fashion. Other embodiments of the invention make it possible to ripen bananas in a sealed container, for example in a conventional ripening room or in a closed container in which the bananas are being transported; and/or to harvest bananas at a later time that it is now possible; and/or to store bananas, after their climacteric, within a desired range of color stages (e.g. within the range most attractive for retail sale) for a longer period than is possible under conventional practice.

Some embodiments of the invention which are particularly suitable for the ripening and/or storage of bananas have been described above. Other aspects of the invention which are particularly suitable for the ripening and/or storage of bananas include the following.

Aspect VII.

A container which is suitable for packaging bananas and which can be sealed around a quantity of bananas, said quantity being at least 4 kg, preferably at least 15 kg, especially 16 to 22 kg, and which, when sealed around the bananas, has an oxygen permeability at 13° C. per kilogram of bananas in the container (abbreviated herein to OP13/kg) of at least 700, preferably at least 1000, particularly at least 1500 ml/atm.24 hrs. In some embodiments, the container has a R ratio at 13° C. of at least 1.3, particularly at least 2, especially at least 3. In some embodiments, the container has an ethylene permeability at 13° C. per kilogram of bananas in the container (abbreviated herein to EtP13/kg) which is at least 2 times, preferably at least 3 times, particularly at least 4 times, the OP13/kg of the container.

It is to be understood that this aspect of the invention includes containers which are as defined above but which are used for the packaging of fruits other than bananas. It is also to be understood that the container as defined above can

be used to ripen fruits by exposing them to any exogenous ERA. When ripening fruits by exposing them to an exogenous ERA other than ethylene, the container preferably has a permeability at 13° C. to that ERA per kilogram of bananas which is at least 2 times, preferably at least 3 times, particularly at least 4 times, the OP13/kg of the container.

Aspect VIII.

A package which comprises

- (a) a sealed container, and
- (b) within the sealed container, bananas and a packaging atmosphere around the bananas; the sealed container having an OP13/kg of at least 700, preferably at least 1000, particularly at least 1500, ml/atm.24 hrs. In some embodiments, the sealed container has a R ratio at 13° C. of at least 1.3, particularly at least 2, especially at least 3.

Aspect IX.

A method of ripening green bananas which comprises

- (A) providing a sealed package which comprises

- (a) a sealed container, and
- (b) within the sealed container, green bananas and a packaging atmosphere around the green bananas, the sealed container having an OP13/kg of at least 700, preferably at least 1000, particularly at least 1500, ml/atm.24 hrs, and preferably having a R ratio 13° C. of at least 1.3, particularly at least 2, especially at least 3, and preferably having an Et13/kg which is at least 3 times, preferably at least 4 times, the OP13/kg of the container; and

- (B) exposing the exterior of the sealed package to an atmosphere containing exogenous ERA.

Aspect X.

A method of ripening green bananas which comprises

- (A) placing in a sealable container,

- (a) the green bananas, and
- (b) a source of exogenous ERA;

- (B) sealing the container around the green bananas and source of exogenous ERA, thus providing a sealed package which comprises

- (a) a sealed container, and
- (b) within the sealed container, the green bananas, the source of exogenous ERA, and a packaging atmosphere around the green bananas, the sealed container having an OP13/kg of at least 700, preferably at least 1000, particularly at least 1500, ml/atm.24 hrs, and preferably having a R ratio 13° C. of at least 1.3, particularly at least 2, especially at least 3, and preferably having an Et13/kg which is at least 3 times, preferably at least 4 times, the OP 13/kg of the container; and

- (C) exposing the bananas in the sealed package to exogenous ERA from the source of exogenous ERA in the sealed container.

Aspect XI.

A method of storing green bananas which comprises

- (A) placing the green bananas in a container which comprises an atmosphere control member which preferably comprises (1) a microporous film, and (2) a polymeric coating, preferably crystalline polymeric coating, on the microporous film;

- (B) sealing the container, thus providing a sealed package which comprises

- (a) a sealed container, and
- (b) within the sealed container, the green bananas and a packaging atmosphere around the green bananas; and
- (C) maintaining the sealed bag at a temperature of 13-18° C.

Aspect XII.

A package which is stored in air and which comprises

- (a) a sealed container, and
- (b) within the sealed container 1 to 6 kg, e.g. 1 to 2.5 kg (2 to 15, e.g. 2 to 5 lb) of bananas which have passed their climacteric and which are at a color stage less than 5, and a packaging atmosphere around the bananas; the sealed container providing a pathway for oxygen and carbon dioxide to enter or leave the packaging atmosphere; the packaging atmosphere preferably containing at least 0.8%, preferably 1.5 to 6%, especially 1.5 to 3% of oxygen and less than 15%, preferably less than 7%, of carbon dioxide in the total quantity of oxygen and carbon dioxide preferably being less than 16%, particularly less than 10%.

Aspect XIII.

A package which comprises

- (a) a sealed container, and
- (b) within the sealed container, bananas and a packaging atmosphere around the bananas; the sealed container including at least one permeable control member which provides a pathway for oxygen, carbon dioxide and ERA to enter or leave the packaging atmosphere and which comprises a gas-permeable membrane comprising
 - (a) a microporous polymeric film, and
 - (b) a crystalline polymeric coating on the microporous film.

Aspect XIV.

A method of ripening green bananas which comprises

- (A) providing a sealed package which comprises
 - (a) a sealed container, and
 - (b) within the sealed container, green bananas and a packaging atmosphere around the green bananas; the sealed container including at least one permeable control member which provides a pathway for oxygen carbon dioxide and ERA to enter or leave the packaging atmosphere; and
- (B) exposing the exterior of the sealed package to an atmosphere containing exogenous ERA.

Aspect XV.

A method of ripening green bananas which comprises

- (A) placing, in a sealable container,
 - (a) the green bananas, and
 - (b) a source of exogenous ERA;
- (B) sealing the container around the green bananas and source of exogenous ERA, thus providing a sealed package which comprises
 - (a) a sealed container, and
 - (b) within the sealed container, the green bananas, the source of exogenous ERA, and a packaging atmosphere around the green bananas;
- the sealed container providing a pathway for oxygen, carbon dioxide and ERA to enter or leave the packaging atmosphere; and
- (C) exposing the bananas in the sealed package to exogenous ERA from the source of exogenous ERA in the sealed container.

Aspect XVI.

A method of storing green bananas which comprises

- (A) placing the green bananas in a sealable container;
- (B) sealing the container, thus providing a sealed package which comprises
 - (a) a sealed container, and
 - (b) within the sealed container the green bananas and a packaging atmosphere around the green bananas; the

sealed container providing a pathway for oxygen and carbon dioxide to enter or leave the packaging atmosphere, and

- (C) maintaining the sealed container at a temperature of 13-18° C.

Aspect XVII.

A method of storing bananas, the method comprising

- (A) providing a sealed package which comprises (a) a sealed container, and (b) within the sealed container, the green bananas and a packaging atmosphere around the green bananas, the sealed container providing a pathway for oxygen and carbon dioxide to enter or leave the packaging atmosphere; and
- (B) storing the sealed package in a controlled atmosphere which contains (i) less than 18% oxygen preferably less than 12% oxygen, particularly less than 9% oxygen, and (ii) more than 2% oxygen, preferably more than 4% oxygen, particularly more than 5% oxygen, the sealed package having an oxygen permeability such that during at least one period of step (B), the oxygen content of the packaging atmosphere reaches a value, which may be in equilibrium value, which is (i) more than 1%, preferably more 2%, and (ii) less than 7%, preferably less than 5%, particularly less than 3.5%.

It is possible for the bananas to ripen under the storage conditions without the use of exogenous ERA. However, the method preferably further comprises

- (C) during or after step (B), exposing the fruits to exogenous ERA, preferably by exposing the exterior of the sealed package to a second controlled atmosphere which contains exogenous ERA, especially a mixture of air and exogenous ethylene, thereby ripening the bananas.

Aspect XVIII.

A method of storing and ripening green bananas, the method comprising

- (A) providing a sealed package comprising (a) a sealed container, and (b) within the sealed container, the green bananas, a packaging atmosphere around the green bananas, and a latent source of exogenous ERA;
- the sealed container providing a pathway for oxygen and carbon dioxide to enter or leave the packaging atmosphere; and
- (B) storing the sealed package (a) under conditions such that ERA is not released from the latent source and (b) in a controlled atmosphere which contains (i) less than 18%, preferably less than 12%, particularly less than 9%, oxygen, and (ii) more than 2%, preferably more than 4%, particularly more than 5%, oxygen, the sealed package having an oxygen permeability such that during at least one period of step (B) the oxygen content of the packaging atmosphere reaches a value which is (i) more than 1%, preferably more 2%, and (ii) less than 7%, preferably less than 5%, particularly less 3.5%; and
- (C) during or after step (B), activating the latent source of exogenous ERA, thereby releasing the exogenous ERA which ripens the bananas.

Aspect XIX.

The use, in packaging bananas, of a containing including at least one permeable control member which provides a pathway for oxygen and carbon dioxide, and which comprises a gas-permeable membrane comprising (1) a microporous film, and (2) a crystalline polymeric coating on the microporous film.

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DETAILED DESCRIPTION OF THE
INVENTION

In the Summary of the Invention above and in the Detailed Description of the Invention, the Examples, and the Claims below, reference is made to particular features (including method steps) of the invention. It is to be understood that the disclosure of the invention in this specification includes all possible combinations of such particular features. For example, where a particular feature is disclosed in the context of a particular aspect or embodiment of the invention, or a particular claim, that feature can also be used, to the extent possible, in combination with and/or in the context of other particular aspects and embodiments of the invention, and in the invention generally.

In describing and claiming the invention below, the following abbreviations, definitions, and methods of measurement (in addition to those already given) are used. OTR is O_2 permeability. COTR is CO_2 permeability. EtTR is ethylene transmission rate. ERATR is ERA transmission rate. OTR, COTR, EtTR and ERATR values are given in $ml/m^2 \cdot atm \cdot 24 \text{ hrs}$; in some cases, the equivalent in $cc/100 \text{ inch}^2 \cdot atm \cdot 24 \text{ hrs}$ is given in parentheses. OTR and COTR values referred to herein can be measured using a permeability cell (supplied by Millipore) in which a mixture of O_2 , CO_2 and helium is applied to the sample, using a pressure of 0.7 kg/cm^2 (10 psi) except where otherwise noted, and the gases passing through the sample were analyzed for O_2 and CO_2 by a gas chromatograph. The cell could be placed in a water bath to control the temperature. The abbreviation P_{10} is used to mean the ratio of the oxygen permeability at a first temperature $T_1^\circ \text{C}$. to the oxygen permeability at a second temperature T_2 , where T_2 is $(T_1 - 10)^\circ \text{C}$. T_1 being 10°C . and T_2 being 0°C . unless otherwise noted. The abbreviation R or R ratio is used to mean the ratio of CO_2 permeability to O_2 permeability, both permeabilities being measured at 20°C . unless otherwise noted. Pore sizes given in this specification are measured by mercury porosimetry or an equivalent procedure. Parts and percentages are by weight, except for percentages of gases, which are by volume; temperatures are in degrees Centigrade, and molecular weights are weight average molecular weights expressed in Daltons. For crystalline polymers, the abbreviation T_o is used to mean the onset of melting, the abbreviation T_p is used to mean the crystalline melting point, and the abbreviation AH is used to mean the heat of fusion. T_o , T_p and ΔH are measured by means of a differential scanning calorimeter (DSC) at a rate of $10^\circ \text{C}/\text{minute}$ and on the second heating cycle. T_o and T_p are measured in the conventional way well known to those skilled in the art. Thus T_p is the temperature at the peak of the DSC curve, and T_o is the temperature at the intersection of the baseline of the DSC peak and the onset line, the onset line being defined as the tangent to the steepest part of the DSC curve below T_p .

The term "comprises" and grammatical equivalents thereof are used herein to mean that other components, ingredients, steps etc. are optionally present. For example, an article "comprising" (or "which comprises") components A, B and C can consist of (i.e. contain only) components A, B and C, or can contain not only components A, B and C but also one or more other components. Where reference is made herein to a method comprising two or more defined steps, the defined steps can be carried out in any order or simultaneously (except where the context excludes that possibility), and the method can include one or more other steps which are carried out before any of the defined steps,

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between two of the defined steps, or after all the defined steps (except where the context excludes that possibility).

The term "controlled atmosphere" is used herein to include an atmosphere produced by adding further gases to an existing atmosphere (including the addition of additional quantities of gas already present in the existing atmosphere, the further gases being added directly to the atmosphere (not passing through a permeable body before reaching the atmosphere).

The term "closed container" is used herein to include a large container, for example a conventional shipping or trucking container which can be loaded onto a ship or a truck, and which is sealed sufficiently to permit a controlled atmosphere to be maintained therein by conventional means well-known to those skilled in the art. The term "shipping or trucking container" is used herein to mean a container which has a volume of at least 8 m^3 and which can be loaded onto a ship or a truck. Such containers are well known to those skilled in the art of storing and transporting fruits and vegetables, and are available in a range of standard sizes.

The term "source of exogenous ERA" is used herein to mean a material, object or system which, either immediately or when activated, generates ethylenic ripening agent. The term "latent source of exogenous ERA" is used herein to mean a material, object or system which is generating little or no ERA, but which can be activated so that it generates substantial quantities of exogenous ERA. The term "residue of a source of exogenous ERA" is used herein to mean a material, object or system which is not a part of a fruit and which remains after exogenous ERA has been generated from a source of exogenous ERA. The residue may be for example (i) a solid material which served as a support for exogenous ERA itself or for one or more precursors of exogenous ERA, or (ii) a liquid residue remaining after a solution of a precursor for an ERA, e.g. 2-chloroethyl phosphonic acid, has been used to generate exogenous ethylene and/or a solid residue resulting from the evaporation of solvent from such a solution. The term "residue of exogenous ERA" is used herein to denote a chemical compound which results from the reaction of exogenous ERA with the fruit being ripened (in which case it is optionally part of the ripe fruit) or with another substance within the sealed package.

The term "ripening" is used herein to mean increasing ripeness; it includes, but is not limited to and generally does not mean, ripening to a point which results in a product which in a retail store would be sold as "ripe". When applied to fruits which ripen through a climacteric, the term "ripening" means ripening the fruits at least through the climacteric. The term "unripe fruits" is used herein to mean fruits which require ripening before they can be sold in retail stores. When applied to fruits which ripen through a climacteric, the term "unripe fruits" means fruits which have not reached their climacteric. The term "banana" is used herein to include plantains.

Where reference is made herein to sealed packages and sealed containers, and to sealing bags and other containers containing biological materials, it is to be understood that the sealing can be, but generally is not, hermetic sealing. Conventional methods for sealing bags and other containers can conveniently be used in this invention. Such conventional methods include, for example, the use of a cable tie to seal the neck of a polymeric bag. A seal made by conventional methods often is not a hermetic seal, and has the advantage that it permits equilibration of the pressures inside and outside the bag. If the container is sealed hermetically, it will generally be desirable to include one or more pinholes

in the container, to achieve such equilibration. The less complete the sealing of the container, the less the influence of the permeability of the container on the packaging atmosphere within it. Thus, even a poor seal may be sufficient, or even desirable, for example when the desired O₂ content of the packaging atmosphere lies between the O₂ content of the atmosphere surrounding the package and the O₂ content of the packaging atmosphere that would result if the seal was a hermetic seal. Under such circumstances, the sealing could be designed to permit a controlled amount of direct exchange between the packaging atmosphere and the atmosphere surrounding the container.

Control Members

The containers used in the present invention preferably, but not necessarily, include at least one atmosphere control member which provides a pathway for O₂ and CO₂, and which preferably comprises a gas-permeable membrane comprising

- (1) a microporous polymeric film, and
- (2) a polymeric coating on the microporous film.

The atmosphere control member is preferably a control member as described in one or more of U.S. Pat. Nos. 6,013,293 and 6,376,032 and International Publication No. WO 00/04787 incorporated by reference herein. The atmosphere control member or members generally provide at least 50%, preferably at least 75%, of the O₂ permeability of the sealed container.

The microporous polymeric film preferably comprises a network of interconnected pores having an average pore size of less than 0.24 micron, with at least 70% of the pores having a pore size of less than 0.24 micron and at least 80% of the pores having a pore size less than 0.15 micron. Preferably the pores in the microporous film constitute 35 to 80% by volume of the microporous film.

The polymeric coating on the control member can optionally comprise a crystalline polymer having a peak melting temperature T_p of -5 to 40° C., e.g. 0 to 15° C. or 10 to 20° C., an onset of melting temperature T_o such that ($T_p - T_o$) is less than 10° C., and a heat of fusion of at least 5 J/g. The polymer can be a side chain crystalline polymer moiety comprising, and optionally consisting of, units derived from (i) at least one n-alkyl acrylate or methacrylate (or equivalent monomer, or example an amide) in which the n-alkyl group contains at least 12 carbon atoms, for example in amount 35-100%, preferably 50-100%, often 80-100%, and optionally (ii) one or more comonomers selected from acrylic acid, methacrylic acid, and esters of acrylic or methacrylic acid in which the esterifying group contains less than 10 carbon atoms. The preferred number of carbon atoms in the alkyl group of the units derived from (i) depends upon the desired melting point of the polymer. For the packaging of biological materials, it is often preferred to use a polymer having a relatively low melting point, for example a polymer in which the alkyl groups in the units derived from (i) contain 12 and/or 14 carbon atoms. The polymer can be a block copolymer in which one of blocks is a crystalline polymer as defined and the other block(s) is crystalline or amorphous. Preferred block copolymers comprise (i) polysiloxane polymeric blocks, and (ii) crystalline polymeric blocks having a T_p of -5 to 40° C.

Other polymers which can be used to coat the microporous film include cis-polybutadiene, poly(4-methylpentene), polydimethyl siloxane, and ethylene-propylene rubber.

The gas-permeable membrane optionally has one or more of the following properties

- (i) a P_{10} ratio, over at least one 10° C. range between -5 and 15° C. or between 10 and 20° C. of at least 2.0 to 2.8;
- (ii) an OTR at all temperatures between 20 and 25° C. of 2,480,000 to 7,000,000 ml/m².atm.24 hr. (160,000 to 450,000 cc/100 in².atm.24 hr); and
- (iii) an R ratio of at least 1.3, preferably 2.0, particularly at least 3.0, especially at least 3.5.

The O₂ permeability of the container at 13° C. per kilogram of fruits therein (OP13/kg) is preferably at least 700, particularly at least 1000, especially at least 1500, ml/.atm.24 hrs. The R ratio of the container at 13° C. is preferably at least 1.3, more preferably at least 2, particularly at least 3. The ethylene permeability of the container at 13° C. per kilogram of fruits therein (EtP/13/kg) is preferably at least 3 times, particularly at least 4 times, the OP13/kg of the container.

The permeability of the container, whether or not it includes an atmosphere control member, can be influenced by perforating the container in order to make a plurality of pinholes therein.

Fruits

This invention is particularly useful for (but is not limited to) the ripening and/or storage of the wide range of fruits which ripen (or undergo other changes, for example, in the case of citrus fruits, de-greening) when exposed to ethylene or another ERA, for example apples, apricots, avocados, bananas, blueberries, cherimoyas, dates, figs, kiwis, mangos, melons, peaches, papayas, pears, peppers, persimmons, and plums (all of which go through a climacteric when they ripen), as well as cherries, grapes, lemons, oranges, tomatoes and strawberries. Some aspects of the invention are especially useful for fruits which in commercial practice are ripened in ethylene-containing ripening rooms, for example avocados, bananas, Bartlett pears, kiwis, mangos, melons, peppers and tomatoes.

Storage of Unripe Fruits

When the invention is being used to store unripe fruits, it is possible to produce desired packaging atmospheres by the selection of containers which, when sealed around the quantities of fruits in question at the selected storage temperature, have appropriate permeabilities to O₂ and CO₂, and by the selection of an appropriate controlled atmosphere around the sealed packages. Those skilled in the art will have no difficulty, having regard to their own knowledge and the contents of this specification, in making appropriate selections to produce a desired packaging atmosphere or to make a desired compromise between (i) the cost and inconvenience of obtaining an entirely satisfactory combination of container and controlled atmosphere, and (ii) the disadvantage of storing the fruits in a packaging atmosphere which is in some ways unsatisfactory.

The table below sets out, for some of the fruits for which this invention is useful, ranges for the concentrations of O₂ and CO₂ which may be used during storage. The invention is, however, useful, for storing these and other fruits outside the ranges stated in the table below.

Fruit	O ₂ content	CO ₂ content
Banana	2-5%	3-7%
Tomato	3-5%	2-3%
Kiwi, nectarine, peach	1-2%	3-5%
Fig, blackberry, blueberry, raspberry, strawberry	5-10%	15-20%

-continued

Fruit	O ₂ content	CO ₂ content
Mango, papaya, pineapple	3-5%	5-8%
Avocado	2-5%	3-10%

Ripening Unripe Fruits by Exposure to Exogenous ERA

In some aspects of the invention, unripe fruits are ripened by exposing it to exogenous ERA while the fruits are in a sealed container. In some embodiments the exogenous ERA enters the packaging atmosphere through the container from the atmosphere surrounding the sealed packages, for example as a result of a

- (i) placing the sealed packages in a conventional ripening room containing exogenous ethylene; or
- (ii) generating an exogenous to ERA-containing atmosphere around the sealed packages while they are in a closed container, e.g. a shipping or trucking container, for example by injecting ethylene gas into the container or by the activation of a source of an exogenous ERA it is within the container but not within the sealed packages; and such source of exogenous ERA could be packed into the container with the sealed packages containing the fruits, for example in the form of packages which release a ripening agent after a desired delay.

In other embodiments, the ERA is generated within each package by activating sources of exogenous ERA placed individually in the sealed packages of unripe fruits. It is also possible to use combination of these embodiments.

The amount of the ERA in the packaging atmosphere should be sufficient to assist ripening. Thus the packaging atmosphere in each of the sealed packages should contain at least 2.5 ppm, typically but not necessarily 100 to 3000 ppm, preferably 250 to 1000 ppm, of ERA. When the exogenous ERA is added to or generated in the atmosphere surrounding the sealed packages, the concentration of ERA in the packaging atmosphere will increase gradually as the exogenous ERA passes through the sealed container at a rate which depends upon the concentration of ERA of the surrounding atmosphere. If, therefore, a rapid initiation of ripening is desired, the concentration of ERA in the atmosphere surrounding the sealed packages is preferably at least 500 ppm particularly at least 1000 ppm. The table below shows the time taken to reach an ethylene concentration of 100 ppm in the packaging atmosphere of a sealed package of bananas according to the invention, when placed in a ripening room containing the indicated concentrations of ethylene.

	Ethylene ppm								
	100	200	300	400	500	700	1000	1500	2000
Time hrs	5.4	1.5	0.9	0.7	0.5	0.4	0.25	0.2	0.1

An advantage of ripening fruits in the sealed container in accordance with the invention, by comparison with conventional ripening by means of a controlled atmosphere directly in contact with the fruits is that the ripe fruits can be substantially less dehydrated. It is believed that this is because ripening takes place in a more controlled fashion, resulting in lower peak temperatures in the fruits, which in turn results in the reduced dehydration. Thus bananas typically lose 3 to 5% of their weight between packaging directly after harvest and being put on retail sales. I have

found that, through use of the present invention this weight loss can be substantially reduced, for example to less than 0.5%. Another benefit, when the ripening is carried out below room temperature, is reduced demand on the refrigeration equipment.

The temperature at which ripening is carried out and the concentration of ERA in the packaging atmosphere influence the rate at which ripening takes place. In general slower ripening results in ripened fruits which remain in a desired range of ripeness for a longer period. On the other hand, rapid ripening may be desired, for example in view of delivery dates required by retail outlets. Thus, the atmosphere around the sealed packages may be above, at, or below ambient temperatures. However, it is generally preferred that the atmosphere should be at a temperature less than 22° C., preferably less than 21° C., for example 16-21° C., or even, for example as a temperature less than 18° C. or less than 60° C., e.g. at 14-15° C.

The atmosphere within the bags will change substantially during the ripening process, as the bananas consume O₂ and generate CO₂. Preferably, the packaging atmosphere, for at least part of the period before the ripening fruits reach their climacteric, contains at least 10% preferably at least 12%, particularly 14 to 19%, of O₂, and less than 10%, preferably less than 4%, of CO₂, with the total quantity of O₂ and CO₂ being less than 20%, preferably less than 17%. For at least part of the period after the ripening fruits have passed their climacteric, the packaging atmosphere preferably contains at least 0.8%, preferably 1.5 to 6%, especially 1.5 to 3%, of O₂, and less than 15%, preferably less than 7%, of CO₂, with the total quantity of O₂ and CO₂ being less than 16%, preferably less than 10%.

When it is desired to ripen fruits while they are being transported, for example on a ship or a truck, ripening by means of a source of exogenous ERA placed within the sealed packages and/or by means of a source of exogenous ERA placed within the large closed container containing the sealed packages, is particularly useful. The ripening can be preceded by a storage period in which there is little or no ripening. The ripening and optional storage process can be controlled so that the fruits are at a desired state of ripeness when they reach their destination. During the process there may be no need to alter the atmosphere around the sealed packages. However, when fruits are stored before they are ripened, it may be desirable to restrict the amount of oxygen which enters the sealed packages during storage, in order to prevent or delay ripening. When the packages can be surrounded by controlled atmosphere (for example while being transported in the hold of a suitably equipped ship), this result can be achieved by placing the sealed packages in a controlled atmosphere containing less than the amount of oxygen present in air (about 21%) for example less than about 12%. The source of exogenous ERA can make ERA available immediately after packaging the bananas, or after a desired delay. Delayed release of ERA can result, for example, from the use of an exogenous ERA source which (i) is activated by an increase in moisture content (for example by water which reaches the ERA source as a result of capillary wicking of water through an intermediate body which separates a water reservoir from the ERA source, or (ii) is associated with (e.g. surrounded by or adsorbed onto) a material which releases ERA or one or more precursors for an ERA, after a set time in response to some outside intervention, for example an increase in temperature.

Any convenient source of exogenous ERA can be used. I have obtained good results using 2-chloroethyl phosphonic acid, which is often referred to herein as 2CPA. 2CPA can be

used in the form of an aqueous solution, for example of concentration 3-4%. The rate at which 2CPA generates ethylene increases with increasing pH of the aqueous solution, which can be adjusted, for example to more than 4, particularly more than 7, by the addition of suitable materials, for example buffer solutions and/or sodium bicarbonate solutions. In one embodiment, a 2CPA solution and any pH adjuster are adsorbed on the same or different absorbent pads, e.g. paper pads, and the pad(s) placed in the bottom of the bag and covered with a polymeric sheet before the bananas are placed in the bag. In another embodiment, a solution of 2CPA is applied to the green bananas, for example by dipping or spraying, before the bananas are placed in the bag.

As in the aspects of the invention which involve ripening in an ethylene-containing atmosphere, the atmosphere within the sealed bags containing the source of ethylene will change during the ripening process. The atmospheres in the bag, for at least part of the periods before and after the climacteric, are preferably as stated above when the bananas are ripened in an ethylene-containing atmosphere.

Quantities of Fruits.

The invention can in principle be used for any quantity of fruits. In some embodiments, for example when the invention is used for storing and/or ripening bananas. However, when the invention is used for ripening and/or storing green bananas, the container preferably contains at least 4 kg, preferably least 15 kg, especially 16 to 22 kg of bananas. In other embodiments, smaller quantities are used, for example to increase the shelf life of bananas at a desired color stage.

EXAMPLES

The invention is illustrated in the following Examples, a number of which are comparative Examples, designated by the letter C before the number of the example. The bananas, bags and control members used in the Examples were as follows.

Bananas

The bananas were Cavendish bananas, from Ecuador in Examples 1A-B, C11-12, 2, C2, 4A-B and C41-42, from Costa Rica in Examples 5 A-C and C5, and from Colombia in the other Examples.

Bags

The large bags were about 0.96 m (38 in.) wide and about 1.2 m (50 in.) long, and were made from polyethylene film about 0.056 mm (2.2 mil) thick (available from Roplast Industries under the tradename RA 3030). The polyethylene film had an OTR at 13° C. of about 2915 (188) and at 22° C. of about 4,650 (300), and EtTR at 13° C. of about 11,400 (735) and at 22° C. of about 18,100 (1,170), an R ratio of about 4.5, and a P10 ratio (between 0 and 10° C.) of about 1.76. The small bags were about 0.3 m (12 in.) wide and about 0.46 m (18 in.) long, and were made from the same polyethylene film.

Control Members

The Type S control members were as described in copending commonly assigned U.S. application Ser. No. 09/121,082, now U.S. Pat. No. 6,548,132, and corresponding International Publication No. WO 00/04787 and comprised a microporous polyethylene film coated with a polysiloxane/SCC block copolymer. The Type S members had an OTR at 13° C. of about 3,803,850 (245,410) and at 22° C. of about 5,000,000 (324,000), an EtTR at 13° C. of about 16,280,000 (1,050,300) and at 22° C. of about 19,500,000 (1,260,000), an R ratio of about 3.8, and a P10 ratio (between 0 and 10° C.) of about 1.8. The microporous polyethylene film con-

tained 50-60% silica, had a thickness of about 0.18 mm (0.007 inch), a tear strength of about 90 g, a porosity of about 65%, an average pore size of about 0.1 micron and a largest pore size of 4-10 microns (available from PPG industries under the tradename Teslin SP 7). The block copolymer was prepared by the reaction of a polydimethyl siloxane terminated one end only by a methacryloxypropyl group (available from Gelest under the tradename MCR M17), 40 parts, dodecyl acrylate, 26.8 parts and tetradecyl acrylate, 33.2 parts, as described in Example A7 of U.S. application Ser. No. 09/121,082, now U.S. Pat. No. 6,548,132, and corresponding International Publication No. WO 00/04787.

The Type A control members were as described in copending commonly assigned U.S. application Ser. No. 08/759,602, now U.S. Pat. No. 6,376,032, and corresponding International Publication No. WO 96/38495, and comprised the same microporous polyethylene film coated with an SCC polymer of dodecyl acrylate, 42 parts, tetradecyl acrylate, 53 parts, and acrylic acid, 5 parts. The Type A members had an OTR at 22° C. of about 1,705,000 (110,000), an R ratio of about 4, and a P10 ratio (between 0 and 10° C.) of about 1.4.

In each Example, the control member was secured to a portion of the bag in which one or more round holes had been cut. The effective area of the control member is about equal to the area of the hole or holes in the portion of the bag to which the control member is attached. However, in Examples 1A-B, C11-12, 2, C2, 3A-D and C31-33, the periphery of the control member was heat sealed to the interior of the bag, thus creating a control member of the kind described in U.S. Pat. No. 6,013,293. In the other Examples, the control member was secured to the exterior of the bag by means of a layer of a pressure sensitive adhesive on the peripheral margin of the control member.

The color stages referred to in the Examples are those accepted by the industry and as shown below.

Color stage	Description
1	95% green
2	80% green, 20% slightly yellow
3	50% yellow, 50% green
4	80% yellow, 20% light green
5	95% yellow, with slight green color at stem and blossom end
6	100% yellow
7	100% yellow with brown sugar spots

Bananas are preferably at color stage 3.5 to 5 when put on retail sale.

Many of the Examples are summarized in Tables 1-8 below. In the Tables, when more than one result is given for a particular Example, this reflects the fact that more than one test was carried out under the same conditions.

Examples 1A-B, C11-12, 2 and C2

Each of these Examples uses a large bag. In Examples C 11,1A-B and 2, each bag has one S-type control member placed under two or more holes in the bag. In Example C11, the control member had an area of 1935 mm² (3 in²) and was placed under two holes, each of diameter 20.6 mm (0.81 in.). In Example 1A, the control member had an area of 6450 mm² (10 in²) and was placed under 6 holes, each of diameter 20.6 mm (0.81 in.). In Examples 1B and 2, the control member had an area of 12,900 mm² (20 in²) and was placed

under 6 holes, each of diameter 28.7 mm (1.13 in). Each bag was packed with about 20 kg (44 lb) of green bananas. The bananas had been harvested at week 11 and maintained at 13-14° C. for about 11 days after harvest before being packed. Except in Examples C12 and C2, excess air was extracted from the bags using a vacuum pump, and the bags were then sealed using tie wraps. In Examples C12 and C2, the bags were left open. The bags were maintained at 13° C. for an extended time, Examples 1A, 1B, C11 and C12 being terminated at day 62, and Examples 2 and C2 being terminated at day 40. The results are given in Table 1 below. In Example 2, traces of ethylene (generated by the ripening of the bananas) remained in the test chamber from Example 1 and caused the bananas to ripen more rapidly than in the otherwise substantially identical Example 1B. This demonstrates the desirability of excluding ethylene when long storage periods are needed (and conversely, the ability to accelerate ripening when desired).

TABLE 1

	Example No.					
	C11	1A	1B	C12	2	C 2
Control member	yes	yes	yes	no	yes	no
Total area of holes in bag under control members (mm ²)	670	2000	3880	—	3880	—
Color stages						
first change at day	>62	44	44	12	26	15
days to change from 3.5 to 4.5	—	—	—	—	4.5	*
days to change from 3.5 to 5	—	**	11	7	#	*
Weight loss (%) on day 26	—	—	—	—	0.35	3.7
on day 41	0.38	0.45	0.60	4.73	—	—
Taste and texture on day 40	—	—	—	—	Exct	◆
on day 62	UGH	Exct	Exct	Overripe	—	—
% O ₂ (approximate)						
at day 7	5.1	11.9	13.8	atm	—	atm
at day 8	—	—	—	atm	14.35	atm
at day 47 (after climacteric)	5.0	0.96	2.2	atm	2.15	atm
% CO ₂ (approximate)						
at day 7	5.3	3.6	3.05	atm	—	Atm
at day 8	—	—	—	atm	3.05	atm
at day 29 (after climacteric)	—	—	—	atm	8.0	atm
at day 47 (after climacteric)	5.3	7.9	8.4	atm	—	atm

UGH unripe, green and hard.
* the bananas had a color of 4.5 when the test was terminated at day 62
Exct excellent taste and texture
test terminated at this point; extrapolation indicates that time to change from color 3.5 to 5 would be 5.9 days.
◆ Bananas removed on day 26 because they were over-ripe.

Examples 3 and C31-33

Each of these Examples uses a large bag. In Examples C31-33 and 3, each bag has one S-type control member placed under one or more holes in the bag. In Example C31, the control member had an area of 967 mm² (1.5 in²) and was placed under a single hole of diameter 20.6 mm (0.81 in.). In Example C32, the control member had an area of 1935 mm² (3 in²) and was placed under 2 holes, each of diameter 20.6 mm (0.81 in.). In Example C33, the control member had an area of 3225 mm² (5 in²) and was placed under 4 holes, each of diameter 19 mm (0.75 in.). In Example 3, the control member had an area of 12,900 mm² (20 in²) and was placed under 6 holes, each of diameter 25 mm (1 in.). In Example C34, the bag did not have a control member. Each bag was packed with about 18.1 kg (40 lb) of green bananas. The bananas had been harvested at week 13, and maintained at 13-14° C. for about 11 days after harvest

before being packed. Except in Example C34, excess air was extracted from the bags using a vacuum pump, and then securely tied (the bags were not, however, as completely sealed as in Examples 1 and 2). In Example C34, the bags were left open. The sealed bags were cooled to about 13° C. and shipped to Gulfport, Miss., and then to San Francisco, Calif., maintaining the temperature at about 13° C. In San Francisco, 36 days after packing, half the bags in each Example were opened, and the other half left intact. All the bags were then exposed to ethylene (500-1000 ppm) in a commercial ripening room for about 24 hours. The bananas in the opened bags ripened rapidly in the expected way; thus by day 43, their color was 6, by day 46 their color was greater than 7, and by day 49, they were overripe. The bags which were still sealed were opened on day 49. The results for the bags opened on day 49 are shown in Table 2 below. These Examples demonstrate that bananas harvested at 13 weeks can be transported in a suitably designed bag, and can

be ripened into an excellent product by exposure to ethylene, either through the bag or after opening the bag.

TABLE 2

	Example No.				
	C31	C32	C33	3	C 34
Control member	yes	yes	yes	yes	no
Total area of hole(s) in bag under control member (mm ²)	335	670	1140	3040	—
Days to change from color stage 3.5 to color stage 5	>8	>8	>8	5.5	DDU
Taste and texture on day 49	SGU	SGU	SGU	Exct	DDU
% O ₂ (approximate) at day 23	8.6	9.8	12.7	15.5	—
at day 46	2.9	0.6	1.8	2.2	—

TABLE 2-continued

	Example No.				
	C31	C32	C33	3	C 34
% CO ₂ (approximate) at day 23	4.45	3.65	3.3	2.85	
at day 46	13.8	11.4	5.0	9.0	

SGU soft, green and unpalatable
DDU dehydrated, decayed and unpalatable by day 47 (day 11 after exposure to ethylene)
Exct excellent taste and texture

Examples 4A, 4B, C41 and C42

Each of these Examples uses a small bag. In Examples 4A-B, each bag has one A-type control member placed over four or five holes in the bag. In Example 4A, the control member had an area of 145 mm² (5.7 in²) and was placed over four holes each of diameter 19 mm (0.75 in.). In Example 4B, the control member had an area of 4516 mm² (7 in²) and was placed over 5 holes, each of diameter 19 mm (0.75 in.). In Example C41, the control member and the holes under it were as in Example 4A, except that the control member was an uncoated microporous film. In Example C42, the bag was intact except for 200 pinholes each about 0.5 mm (26 gauge) in diameter. Each bag was packed with about 1.35 kg (3 lb) of green bananas which had been maintained at 13-14° C. for about 11 days after harvest. Except in Example C42, excess air was extracted from the bags using a vacuum pump, and the bags were then securely tied. In Example C42, the bags were left open. After three days, to allow the packaging atmosphere to equilibrate, the bags were exposed to ethylene (500-1000 ppm) in a ripening room. The results are shown in Table 3 below. These Examples demonstrate that small quantities of bananas can be ripened in a suitably designed bag, and can remain in the bag in excellent condition for several days longer than bananas exposed to the air.

TABLE 3

	Example No.			
	4A	4B	C41	C42
Control member	yes	yes	◆	no
Total area of holes in bag over control member (mm ²)	1140	1425	1140	—
Color stage on day 10 after ethylene treatment	4.0	4.4	7.0	6.8
Weight loss (%) on day 10 after ethylene treatment	0.57	0.72	1.05	0.61
Taste & texture on day 10 after ethylene treatment	Exct	Exct	Over-ripe	Over-ripe

◆ uncoated microporous film
Exct excellent taste and texture

Examples 5A, 5B, 5C and C5

These Examples show that the bananas generate heat more evenly when ripened in a container including an atmosphere control member. In each Example, a large bag was packed with about 18.1 kg (40 lb.) of green bananas. The green bananas had been harvested 13 days previously and had been stored at 13-14° C. since harvest. A temperature sensor (available from Sensitech, Beverly, Mass., under the tradename Temptale P) was inserted into one banana in each bag. In each of Examples 5A, 5B and 5C, the bag had

two S-type control members, each having an area of 11,300 mm² (17.5 in²). Each control member was placed over a single hole in the bag, the hole having an diameter of 70 mm (2.75 in.) in Example 5A, 74.4 mm (2.93 in.) in Example 5B, and 78.7 mm (3.1 in.) in Example 5C. In Example C5, the bag was perforated so that the bananas were surrounded by air. The bags were then sealed with rubber bands. The sealed bags were placed in a refrigerated room at about 13° C. After about 84 hours, the temperature of the room was raised to about 16.7° C. and after about 12 hours, an ethylene generator was used to provide an initial ethylene concentration in the room of 500-1000 ppm. About 24 hours after the generation of ethylene had begun, the room was vented. The temperature of the bananas was monitored for about 15 days, and reached a peak at about 60 hours after the generation of ethylene had begun. At that time, the concentration of O₂ and CO₂ was measured. The results are shown in Table 4 below. It will be seen that the peak temperature was substantially lower in the bags containing control members than in the perforated bag.

TABLE 4

	Example No.			
	5A	5B	5C	C5
Control member	yes	yes	yes	no
Total area of holes in bag under control members (mm ²)	7700	8700	9700	—
Temperature (° C.) of bananas 12 hrs after temperature of room was set to 16.7° C.	16.3	15.9	15.7	16.6
Peak Temperature ° C.	21.2	21.1	20.9	23.9
Difference between peak temperature and 16.6° C.	4.9	5.3	5.2	7.3
% O ₂ 60 hours after injection of ethylene	2.2	1.75	1.9	20.95
% CO ₂ 60 hours after injection of ethylene	7.95	6.1	7.4	0.03

Examples 6 A-E

Each of these Examples uses a large bag having two S-type control members, each control member having an area of 11,300 mm² (17.5 in²). Each control member was placed over seven holes in the bag, each hole of diameter 25.4 mm (1 in). A paper pad about 300×400 mm (12×16 in.) impregnated with an aqueous solution of 2CPA (3.9%) was placed in the bottom of each bag and covered with a sheet of polyethylene. The amount of the solution varied from Example to Example, and is shown in Table 5 below. About 18.1 kg (40 lb.) of green bananas were then placed in each bag, and the bags were sealed with rubber bands. The green bananas had been maintained at 13-14° C. for about 11 days after harvest. The sealed bags were left in a cold room at 13-14° C. The color stage of the bananas was monitored, and Table 5 below shows the time in days taken to reach color stages 4 and 5.5.

TABLE 5

	Example No.				
	6 A	6B	6C	6D	6E
Control member	yes	yes	yes	yes	yes
Total area of holes in bag under control members (mm ²)	7100	7100	7100	7100	7100

TABLE 5-continued

	Example No.				
	6 A	6B	6C	6D	6E
mL of 3.9% 2CPA solution on paper pad	30	50	100	200	500
Days to color stage 4	11	10.8	10.6	11	9.6
	*	20.4	20.1	12	12
	*	10.5	11	11	11

* this color stage had not been reached when the experiment was terminated after 27 days.

TABLE 5-continued

	Example No.				
	6 A	6B	6C	6D	6E
Days to color stage 5.5	17.5	*	17.4	16	16.1
	*	*	24.2	16	16.9
	*	17.5	17.4	16	16.3
Days from color stage 4 to color stage 5.5	6.5	—	6.8	5	6.5
	—	—	3.1	4	4.9
	—	7	6.4	5	5.3

* this color stage had not been reached when the experiment was terminated after 27 days.

Examples 7 A-D and C71-74

The procedure of Example 6 was followed except for the changes noted below.

1. In Examples 7A-D, there was a single hole, diameter 82.5 mm (3.25 in.), under each of the two control members. The total area of the holes was 10,700 mm².
2. In Examples 7A, 7B and 7C and in comparative Examples C72 and C73, a paper pad impregnated with 0.1N NaHCO₃ solution was placed adjacent to the paper pad impregnated with 2CPA solution, thus increasing the pH of the 2CPA solution and increasing the rate at which ethylene was generated. The amount of the NaHCO₃ solution varied from Example to Example as shown in Table 6 below.

3. In Examples 7D and C74, 2CPA was not used, but three days after packing, the bags were exposed to ethylene for 24 hours in a conventional ripening room at 16.7° C. and containing 500-1000 ppm of ethylene.
 4. Comparative Examples C71-74 were carried out in which no ethylene was used (C71), or the bag was sealed but did not have a control member (C 72-73), or the bag was not sealed (C74).
 5. The ethylene concentration in the bags was measured at various times after packing
- The results obtained are shown in Table 6 below.

TABLE 6

Example No.	7A	7B	7C	7D	C71	C72	C73	C74
Control member	yes	yes	yes	yes	yes	no	no	no
mL 3.9% 2CPA solution	30	30	30	no	no	30	30	no
mL 0.1N NaHCO ₃	15	30	60	no	no	13	30	no
Exposed to ethylene in ripening room	no	no	no	yes	no	no	no	yes
Days to color stage 4	12	10.2	6.2	6.5				4.2
	12.5	10.2	9.4	6.5				4.5
	15	8.4	9.8	7.1				4.5
Days to color stage 5.5	*	*	9.5	11.5				6.6
	*	*	12.5	12				7
	*	*	12.9	12.3				7.2
Days from color stage 4 to color stage 5.5	—	—	3.3	5				2.4
	—	—	3.1	5.5				2.5
	—	—	3.1	5.2				2.7
Color after 15 days ppm ethylene after					2	2	2	
0 hrs	0.47	4.11	8.65			5.72	10.7	
7 hrs	0.58	2.36	10.04			7.81	13.35	
72 hrs	0.68	1.94	6.66			10.8	20.51	
79 hrs	—	3.28	4.7			59.43	16.65	
% O ₂ after 15 days	3.73	3.97	3.72			0.21	0.34	
% CO ₂ after 15 days	6.23	6.2	4.67			27.3	25.5	

* this color stage had not been reached when the experiment was terminated.

Examples 8A-J and C81-83

Examples 8A-J and C 81-83 followed the same procedure as Examples 7A-C and C71-74 except for the changes noted below.

1. The ethylene, O₂ and CO₂ concentrations were determined at different times.
 2. In some of the examples, the second paper pad was impregnated with 30 mL of an aqueous buffer solution (i) containing potassium phthalate and having a pH of 4, (ii) containing dibasic sodium phosphate, monobasic potassium phosphate, sodium chromate and potassium dichromate, and having a pH of 7, or (iii) containing sodium carbonate and sodium bicarbonate and having a pH of 10. These buffer solutions are available from Orion Research Inc., Beverley, Mass. USA
 3. In Examples 8H and C83, the bag was taken to the ripening room 3 days after packing
 4. In Example 8G, the sealed bags were left in a room at about 21° C. (in the other Examples, the room was at 13-14° C.).
 5. In Example C83, the bag was not sealed.
- The results are shown in Table 7 below.

TABLE 7

	8A	8B	8C	8D	8E	8F	8G	8H	C81	C82	C83
Control member	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	no
mL 3.9% 2CPA solution	30	30	30	30	30	30	30	no	no	30	no
mL 0.1N NaHCO ₃	no	no	no	45	60	75	60	no	no	60	no
30 mL of buffer having	pH 4	pH 7	pH 10	no	no	no	no	no	no	no	no
Exposed to ethylene	no	no	no	no	no	no	no	yes	no	no	yes
in ripening room											
Days to color stage 4	11.9	15.4	13.1	9.4	8.5	9.0	8.2	7.7	*	*	3.7
	13.0	11.3	11.5	9.0	9.3	8.1	7.6	—	—	—	3.9
	14.3	10.1	10.8	10.1	8.0	8.1	6.7	10.6	—	—	3.9
Days to color stage 5.5	—	—	—	15.7	13.8	12.4	14.8	14	*	*	5
	—	15.3	—	12.3	13.1	11.4	12.2	—	—	*	6
	—	—	16.6	15	11.9	11.4	9.0	*	—	—	6
Days from color stage 4	*	*	—	6.3	5.3	3.4	6.2	6.3	—	—	1.3
to color stage 5.5	*	4	—	3.3	3.8	3.3	4.6	—	—	—	2.1
	*	*	5.8	4.9	3.9	3.3	2.3	—	—	—	2.1
ppm ethylene after 24 hrs	0.88	1.67	1.37	3.25	4.39	5.58	10.9	0.49	0.39	39.5	0
% O ₂ after 8 days	3.72	5.58	2.93	3.2	2.39	2.52	1.95	2.97	17	0.3	—
% CO ₂ after 8 days	4.73	4.7	5.3	4.97	5.13	5.47	7.97	4.73	1	17.6	—

* this color stage had not been reached when the experiment was terminated after 17 days.

Examples 9A-C and C91-92

The procedure of Example 6 was followed, except for the changes noted below.

1. There was a single hole, diameter 82.5 mm (3.25 in.), under each control member. The total area of the hole was 5350 mm².

2. No 2CPA-impregnated paper pad was placed in the bag.

3. The bananas, before being packed into the bag, were dipped into a dilute aqueous solution of 2CPA. The concentration of the 2CPA varied from Example to Example as shown in Table 8 below.

4. Comparative Examples C91 and C92 were carried out in which the bag did not have a control member (C91) or the bananas were not treated with 2CPA solution (C92). Comparative Example C91 is the same as the comparative Example C71.

The results obtained are shown in Table 8 below.

TABLE 8

	Example No.			
	9A	9B	C91	C92
Control Member	yes	yes	no	yes
Concentration of 2CPA (ppm)	1116	128	1116	0

TABLE 8-continued

	Example No.			
	9A	9B	C91	C92
Days to color stage 4	11.9	14.6	*	*
	10	*	*	*
	11.9	11	*	*
Days to color stage 5.5	*	*	*	*
	*	*	*	*
	*	*	*	*

* this color stage had not been reached when the experiment was terminated after 27 days

Table 9 below shows, for each of the bags in Examples 5A-C, 6A-E and 7A-E, the permeability of the bag to O₂ and to ethylene (“Et” in Table 9), and the respective contributions of the control member and the remainder of the bag. For this calculation, the size of the bag, after sealing, was assumed to be 0.96×1.04 m (38 in.×41 in.), i.e. to have a total area of 2 m² (3115 in²).

TABLE 9

Example No.	Perm. of bag (mL/atm.24 hr) at 13° C.	Perm. of bag at 13° C./kg of bananas	Hole area (m ²)	Perm. Of ACM at 13° C.	Perm. of rest of bag at 13° C.
C11	O ₂ 8,450 Et 36,000	O ₂ 470 Et 2,000	0.000670	O ₂ 2,550 Et 10,900	O ₂ 5,900 Et 25,100
1A	O ₂ 13,500 Et 57,650	O ₂ 745 Et 3,185	0.002000	O ₂ 7,600 Et 32,550	O ₂ 5,900 Et 25,100
1B	O ₂ 20,650 Et 88,250	O ₂ 1,140 Et 4,875	0.003880	O ₂ 14,750 Et 63,130	O ₂ 5,900 Et 25,100
2	O ₂ 20,650 Et 88,250	O ₂ 1,140 Et 4,875	0.003880	O ₂ 14,750 Et 63,130	O ₂ 5,900 Et 25,100
C31	O ₂ 7,200 Et 30,650	O ₂ 395 Et 1,695	0.000335	O ₂ 1,300 Et 5,500	O ₂ 5,900 Et 25,100
C32	O ₂ 8,500 Et 36,000	O ₂ 470 Et 2,000	0.000670	O ₂ 2,550 Et 10,900	O ₂ 5,900 Et 25,100
C33	O ₂ 10,250 Et 43,650	O ₂ 565 Et 2,400	0.001140	O ₂ 4,350 Et 18,550	O ₂ 5,900 Et 25,100
3	O ₂ 17,450 Et 74,600	O ₂ 965 Et 4,120	0.003040	O ₂ 11,550 Et 49,500	O ₂ 5,900 Et 25,100

TABLE 9-continued

Example No.	Perm. of bag (mL/atm.24 hr) at 13° C.	Perm. of bag at 13° C./kg of bananas	Hole area (m ²)	Perm. Of ACM at 13° C.	Perm. of rest of bag at 13° C.
5 A	O ₂ 35,000 Et 149,800	O ₂ 1,935 Et 8,280	0.007700	O ₂ 29,100 Et 124,700	O ₂ 5,900 Et 25,100
5B	O ₂ 39,000 Et 166,650	O ₂ 2,155 Et 9,200	0.008700	O ₂ 33,100 Et 141,550	O ₂ 5,900 Et 25,100
5C	O ₂ 42,900 Et 183,550	O ₂ 2,370 Et 10,150	0.009700	O ₂ 37,000 Et 158,450	O ₂ 5,900 Et 25,100
6 A-E	O ₂ 32,840 Et 140,500	O ₂ 1,815 Et 7,750	0.007100	O ₂ 26,940 Et 115,400	O ₂ 5,900 Et 25,100
7 A-E	O ₂ 46,500 Et 199,200	O ₂ 2,570 Et 11,000	0.010700	O ₂ 40,600 Et 174,100	O ₂ 5,900 Et 25,100

15

Example 10

Three trials were carried out to compare bananas transported and ripened (a) conventionally in 12 conventional bags as controls, and (b) in accordance with the invention in 36 bags having atmosphere control members. Each bag was supported by a cardboard box. The conventional bags were about 1 m. (38.5 in.) by 1.25 m. (49.5 in.) and were made of polyethylene film about 0.18 mm (0.0007 in.) thick. Each conventional bag was perforated with about 312 holes, each about 12.5 mm (0.5 inch) in diameter. The bags used in accordance with the invention were about 1 m. (39.75 in.) by 1.2 m (46.25 in.) and were made of a film of a blend of polyethylene and ethylene/vinyl acetate copolymer about 0.05 mm (0.002 in.) thick. Each bag had two S-type atmosphere control members, each control member being about 145 mm (5.625 in.) by 120 mm (4.72 in.) and being secured to the exterior of the bag by a layer of contact adhesive about 11 mm (0.44 in.) wide around its periphery. Under each atmosphere control member, the bag had seven holes each about 25 mm (1 in.) in diameter. The effective area of the control member was about equal to the area of the holes in the bag.

In Columbia, each bag was packed with about 20 kg. of green, freshly harvested bananas. The necks of the bags of the invention were sealed with rubber bands. The necks of the conventional bags were not closed. The bags were weighed and then transported at about 14.5 Co. (58° F.) to Watsonville, Calif., U.S.A., where, 13 days after harvest, they were placed in a commercial ripening room containing ethylene for 24 hours at about 16.5° C. (62° F.). The room was then vented and maintained at about 16.5° C. (62° F.) for the next 24 hours, at about 15.5° C. (60° F.) for the next 48 hours, and at about 14.5° C. (58° F.) for the next 24 hours. The bananas were then maintained at about 21° C. (70° F.). The table below shows the average weight loss of the bags, and the color of the bananas in the bags, on the day indicated. The sealed bags were not opened until the day indicated in the table below.

20

25

30

35

40

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	Trial 1		Trial 2		Trial 3	
	Inven- tion	Con- trol	Inven- tion	Con- trol	Inven- tion	Con- trol
Days after harvest	11	9	10	9	10	9
Weight loss (%)	0.44	5.17	0.4	4.6	0.07	4.66
Color	5.25	7	5.75	9	5.3	7

- What is claimed is:
1. A method of storing and/or ripening a respiring biological material, the method comprising
 - (A) providing a sealed package comprising
 - (a) a sealed container, and
 - (b) within the sealed container, at least 4 kg of a respiring biological material surrounded by a packaging atmosphere, the sealed container including an atmosphere control member which provides a pathway for oxygen and carbon dioxide to enter or leave the packaging atmosphere, and
 - (B) exposing the exterior of the atmosphere control member to a first atmosphere containing oxygen,
 - (C) exposing the exterior of the atmosphere control member to a second atmosphere containing oxygen, the first and second atmospheres differing by at least 1% in their content of at least one gas which will pass through the atmosphere control member into the packaging atmosphere and which is an insecticide, a fungicide or a mold-inhibiting compound.
 2. A method according to claim 1 wherein the fruit is selected from the group consisting of apples, apricots, avocados, bananas, blueberries, cherimoyas, dates, figs, kiwis, tomatoes, pineapples, cherries, grapes, lemons, oranges, raspberries, strawberries, mangos, melons, peaches, nectarines, papayas, pears, peppers, persimmons and plums.
 3. A method according to claim 1 wherein the fruit is blueberries.
 4. A method according to claim 1 wherein the fruit is bananas.
 5. A method according to claim 1 wherein the atmosphere control member consists of a membrane which comprises a microporous film and a polymeric coating on the microporous film and which has an OTR of at least 50,000 cc/100 inch² .atm.24hrs.

* * * * *